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Predicting Density and Refractive Index of Ionic Liquids

Mercedes G. Montalbán, Mar Collado-González,
F. Guillermo Díaz-Baños and Gloria Vllora

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Abstract

The determination of the physicochemical properties of ionic liquids (ILs), such as density and refractive index, is essential for the design of processes that involve ILs. Density has been widely studied in ILs because of its importance whereas refractive index has received less attention even though its determination is rapid, highly accurate and needs a small amount of sample in most techniques. Due to the large number of possible cation and anion combinations, it is not practical to use trial and error methods to find a suitable ionic liquid for a given function. It would be preferable to predict physical properties of ILs from their structure. We compile in this work different methods to predict density and refractive index of ILs from literature. Especially, we describe the method developed by the authors in a previous work for predicting density of ILs through their molecular volume. We also correlate our experimental measurements of density and refractive index of ILs in order to predict one of the parameters knowing the other one as a function of temperature. As the measurement of refractive index is very fast and needs only a drop of the ionic liquid, this is also a very useful approach.

Keywords: ionic liquids, density, refractive index, ionic volume, molecular volume, prediction, correlation

1. Introduction

Ionic liquids (ILs) are organic salts with low melting point so most of them are liquid at room temperature. During the last years, scientists and engineers have shown a huge interest for ILs in research and industrial fields because of their capacity for being chemical and biochemical reaction media. ILs are also of interest because they can be considered a new group of

polar and nonaqueous solvents. Their most important advantage as solvents is that they possess negligible vapor pressure [1]. For that, they are well known as “green solvents” compared to conventional volatile organic compounds (VOCs). Other relevant properties of the ILs are that they are highly stable from the chemical and thermal points of view. However, ILs are mainly valued because of the possibility of modulating their physical and chemical properties, such as melting point, viscosity, density, hydrophobicity and polarity by selecting the appropriate anion and cation and, in this way, they can be used for a specific application. For this reason, some authors have called them “designer solvents.” Hence the number of different combinations of anions and cations that can be chosen to form potential ILs is enormous [2]. Some years ago, Álvarez-Guerra and Irabien [3] claimed that “more than 10^6 different ILs may be synthesized, with 10^{12} binary combinations and 10^{18} ternary systems possible,” while the number of traditional solvents widely used in industry is around a few hundred. The excellent properties of the ILs permit their application in many different fields such as synthesis, catalysis, electrochemistry, separation technology, analytical chemistry and nanotechnology [4].

In order to design processes involving ILs, it is essential to determine and understand some of their physicochemical properties, such as density and refractive index [5]. On the one hand, density of ILs is related to the mechanics and engineering components of a process and is usually used to determine parameters like rates of liquid-liquid phase separation, mass transfer, power requirements of mixing and pumping and equipment sizing [6]. In fact, density of ILs is necessary to solve material or energy balance equations of chemical processes in industry [7]. On the other hand, refractive index of ILs is more linked to specific chemical properties like the structuredness, polarity and relative hydrogen bonding donating and accepting ability which help to determine solubilities, partition constants and reaction rates [8]. In general, refractive index of a compound is especially used to verify a material and check its purity, or to determine the concentration of a mixture. It is also related to the forces between molecules or their behavior in solution [9] and can be easily correlated with certain properties of the material such as the dielectric constant, density and surface tension by means of thermodynamic equations [10].

We compile in this chapter different methods to predict density and refractive index of ILs from the literature. Especially, we describe the method developed by the authors in a previous work for predicting density of ionic liquids through their molecular volume. We also correlate our experimental measurements of density and refractive index for a set of ionic liquids in order to predict one of the parameters knowing the other one as a function of temperature [6].

2. Prediction methods of density of ionic liquids

Density (ρ) is defined as the mass (m) per volume unit (V), $\rho = m/V$, and is one of the most relevant physical properties of a chemical compound.

As it has been mentioned before, nowadays the possible number of combinations of cation/anion to form ILs is huge. For this reason, it is almost impossible to measure experimentally

the density of all the feasible ILs. In addition, it is not worthwhile to use trial and error methods to find the suitable IL for a specific application. Therefore, developing reliable predictive methods and correlations to estimate the density of ILs in a wide range of temperature is essential. Furthermore, this kind of method allows a better understanding of the influence of the structure of the ILs on the density and on other physicochemical properties [7].

During the last years, authors have developed different methods to estimate density of ILs. We have compiled in this chapter published studies concerning methods to predict or estimate density of ILs according to the classification established by Paduszyński and Domańska [7]. Briefly, some authors have used methods based on quantitative structure-property relationships (QSPRs) [11–15] and on artificial neural networks (ANNs) [16–18]. Other authors have developed estimation methods for density of ILs by adopting equation of state (EoS) [19–29]. There are also some studies in which the estimation of density of ILs is carried out by group contribution methods (GCMs) [6, 7, 10, 30–37] and correlations between density and other properties such as refractive index, molar refraction or surface tension [6, 38–42]. In order to improve the predicting capabilities, it is usual to find in the literature a combination of methods included in different categories of this classification.

2.1. Estimation by quantitative structure-property relationships (QSPRs)

A QSPR model is a mathematical model that links the structure-derived features of a chemical compound to a physicochemical property. They are based on quantum chemistry calculations. This is their great advantage and, at the same time, their main drawback. While virtually any imagined compound can be studied with no previous experimental knowledge, usually the calculations are not easy and only can be developed by very specialized research groups.

In the literature, we can find several QSPR models to predict density of ILs. Trohalaki et al. [13] developed a QSPR model by the use of CODESSA software. They use three types of descriptors (electrostatic, quantum mechanical and thermodynamic) in order to predict the density of triazolium-based ILs. Palomar et al. [15] determined the density of 40 imidazolium-based ILs using COSMO-RS. In this model, thermodynamic data are obtained from the molecular surface polarity of the individual compounds of the mixture. A year later, they combined COSMO-RS with ANN to get a computational approach with a new descriptor which was useful to simulate the density of 45 imidazolium-based ILs [14]. Interestingly, this approach allows them to propose a design strategy which introduces the desired IL properties as input into inverse neural networks to obtain a selection of counterions. Lazzús [18] used a QSPR model with 11 descriptors based on semiempirical calculations to estimate the density of ILs as a function of temperature and pressure. Specifically, the range of temperature and pressure was 258–393 K and 0.09–207 MPa, respectively. Finally, El-Harbawi et al. [11] proposed a new QSPR model using MATLAB™ software for the development of the algorithm and the same molecular descriptors used by Shen et al. [24]. The code was written based on a combination of multiple linear regression and polynomial equation.

2.2. Estimation by artificial neural networks (ANNs)

ANN is an especially efficient computer algorithm to approximate any function with a finite number of discontinuities by learning the relationships between input and output vectors [43]. ANNs are usually suitable to model chemical properties whose behavior is highly nonlinear because nonlinear relationships are well described with ANN. The predicting capabilities of this method depend on the quality of the algorithm for learning and very importantly on the quality, quantity and nature of experimental (or calculated) data used for the learning process. Some authors have developed approaches to estimate density of ILs based on ANN combined with a GCM.

Properties of chemical compounds like boiling point, critical temperature, critical pressure, vapor pressure, heat capacity, enthalpy of sublimation, heat of vaporization, density, refractive index, surface tension, viscosity, thermal conductivity, and acentric factor have been analyzed by ANN in the literature [44]. For instance, Valderrama et al. [17] proposed a combined GCM + ANN method which divides the molecule in defined groups but instead of determining the value of the group contributions, an ANN is used to get the relationship between the dependent and independent variables. In this way, the relationship between density and molecular structure was determined. Lazzús [16] also proposed in a first paper another combined (GCM + ANN) method, which uses a feedforward backpropagation neural network. It is shown that this network is very efficient in representing nonlinear relationships among properties. Specifically, the network, which was programmed with the software MATLAB, consists of a multilayer network, in which the flow of information spreads forward through the layers while the propagation of the error is back. In this way, he predicted the density of 72 ILs as a function of temperature and pressure. Later, Lazzús [18] published the estimation results obtained with another similar model replacing standard backpropagation with particle swarm optimization (PSO) because some authors had shown that PSO-based ANN led to a better training performance and predicting capacity and a faster convergence rate than the standard backpropagation algorithm. Briefly, PSO is a population-based optimization tool, where the system is initialized with a population of random particles and the algorithm searches for optima by updating generations [45]. In a PSO system, each particle is “flown” through the multidimensional search space, adjusting its position in search space according to its own experience and that of neighboring particles. The particle therefore makes use of the best position encountered by itself and that of its neighbors to position itself toward an optimal solution. The performance of each particle is evaluated using a predefined fitness function, which encapsulates the characteristics of the optimization problem [46].

2.3. Estimation by equation of state (EoS)

Equations of state are well known for determining the relationship between pressure, temperature, volume and composition of components providing a theoretical way to calculate some physical properties such as density. Therefore, some equations of state have been used to estimate density of ILs in the literature. Usually the proposed EoS contains some constants whose values have been obtained by previous fitting of the available experimental results. The main advantage is the simplicity in the use of these methods but a possible drawback is that

to obtain the density of the desired compound usually some previous experimental (or calculated) data of certain critical properties (temperature, pressure, volume, ...) are needed.

Goharshadi and Moosavi [19] proposed a simple EoS (called GMA EoS) to predict the density of phosphonium and imidazolium-based ILs at different temperatures and pressures. Valderrama and Zarricueta [21] used ten expressions based on the corresponding state principle to estimate the density of ILs and analyzed one of them in depth to obtain a new generalized, accurate and simple model using only the critical properties and the molecular weight of the ionic liquid. As several authors have claimed that the dependence between density and temperature is linear, the proposal of Valderrama and Zarricueta was to linearize the Valderrama and Abu-Sharkh model [47] to end up with a simple and totally predictive model, the linear generalized model, to estimate the density of ILs with acceptable accuracy.

Ji and Adidharma [26] modeled the density of three families of ILs ($[C_n\text{mim}][\text{Tf}_2\text{N}]$, $[C_n\text{mim}][\text{BF}_4]$ and $[C_n\text{mim}][\text{PF}_6]$) in a wide temperature and pressure range by the usage of a model published in previous works [48–50]. Specifically, this model uses a heterosegmented statistical associating fluid (hetero-SAFT) equation of state which can predict the properties of an ionic liquid based on the information of its alkyl substituent, cation head and anion. However, this model does not taken into account the electrostatic interactions. On the contrary, Wang et al. [23, 27] included an electrostatic term to residual Helmholtz energy expressed by mean spherical approximation (MSA) and they improved the results.

Abildskow et al. [22] used the statistical mechanical fluctuation solution theory to develop two models which provide a direct connection between integrals of the molecular direct correlation function and isothermal derivatives of pressure and density. In this way, they can predict densities of ILs at elevated pressures.

Shen et al. [24] extended the Valderrama and Robles [51] group contribution model for the critical properties to the estimation of densities of ILs at different temperatures and pressures representing the critical properties by the modified the Lydersen-Joback-Reid group contribution method and predicting the density by the Patel-Teja (PT) equation of state.

Patel and Joshipura [25] used a simple correlation presented by Nasrifar and Moshfeghian [52] in conjunction with the predictive-Soave-Redlich-Kwong (PSRK) equation of state to estimate density of ILs.

More recently, Mahboub and Farrokhpour [28] developed a molecular modeling of ILs incorporating the perturbed thermodynamic linear Yukawa isotherm regularity (LYIR) equation of state, which is derived based on an effective nearest neighboring pair attractive interaction of the Yukawa potential. They used this model to predict the densities of ILs up to high pressures (35 MPa) and in the temperature range 293.15–393.15 K. To use the LYIR for ILs, a simple molecular model was proposed to describe their molecular structure, in which they were considered as a liquid consisting of the ion pairs moving together in the fluid, and each ion pair was assumed to be a one-center spherical united atom. Farzi and Esmailzadeh [29] used the Esmailzadeh-Roshanfekar EoS obtained in a previous paper [53] to predict density of ILs. This EoS is based on the Patel-Teja EoS and Peng-Robinson EoS and offer better results than these two equations especially near the critical areas.

2.4. Estimation by group contribution methods (GCMs)

Other authors have preferred to develop GCMs to estimate the density of ILs. First of all, we will revise briefly the published studies in the literature and after that we will detail our own predictive method based on a GCM. In these methods, the desired property is obtained as individual contribution of each of the components of the final compound. Then, predictions are obtained using available simple equations. The main drawback of these methods is that their predictive capability depends on previous experimental (or calculated) data. With some exceptions, it is impossible to predict density if no data are available for both of the components of an ionic liquid. On the other hand, usually good predictions can be obtained very easily for any combination of known counterions in a few minutes.

Slattery et al. [32] supported that a strong relationship exists between molecular volumes and density. Thus they described this relationship and predict the density of ILs only from their molecular volumes and an anion-dependent correlation. They considered the molecular volume as the sum of the individual contributions of the anion and the cation. Ye and Shreeve [36] widened a predictive method proposed by Jenkins et al. [54] for estimation of thermochemical radius and closed packed volume of single ions and used it as GCM for ILs. The method provided good density prediction results but, unfortunately, is limited to room temperature and ambient pressure. To solve this disadvantage, Gardas and Coutinho [31] extended this method estimating three coefficients independent of the ionic liquid which take into account the influence of temperature and pressure on the molecular volume. In this way, they can predict the density of ILs in a wide range of temperature (273.15–393.15 K) and pressure (0.10–100 MPa). Jacquemin et al. [34, 35] studied the suitability of GCMs to predict density of ILs. The study was based on an assumption proposed by Rebelo et al. [55, 56] that the molar volume of the ILs can be obtained from the effective molar volumes of the ions considering the ionic liquid as an “ideal” mixture. Qiao et al. [30] introduced the interaction between several substitutes on the same center in the partition of groups. For that, the same group structure attached to different substitutes may have different group values. Paduszyński and Domańska [7] proposed a simple and generalized correlation to estimate the density of ILs as a function of temperature and pressure. They divided the ILs in 177 functional groups which are classified in three subgroups: cation cores, anion cores and substituents. In this way, they obtained the group contributions to molar volume for each of the functional groups and the universal coefficients describing the relationship pressure-density-temperature. Lately, Keshavarz et al. [37] provided a simple correlation to predict density of ILs based on their size, structure and types of cations and anions. They introduced two correcting terms which take into account the effect that some specific cations and anion may have in the ionic packing leading to its increase or decrease and hence affect to the density values. Finally, Kermanioryani et al. [33] found new group contribution parameters using the Gardas and Coutinho model [31] to predict the density of ILs more accurately.

Recently, we have proposed our own method to predict density of ILs [6]. It can be considered as a GCM and it is based on the prediction of the molecular volume of ILs from the ionic volume. It will be described in detail in the following paragraphs.

<i>T</i> /K	V_m/nm^3	$\alpha_p \times 10^{-4}/\text{K}^{-1}$	V_m/nm^3	$\alpha_p \times 10^{-4}/\text{K}^{-1}$	V_m/nm^3	$\alpha_p \times 10^{-4}/\text{K}^{-1}$
	[emim⁺][BF₄⁻]		[bmim⁺][BF₄⁻]		[hmim⁺][BF₄⁻]	
293.15	0.2561	5.93	0.3119	5.96	0.3676	6.06
303.15	0.2577		0.3134		0.3698	
313.15	0.2592		0.3152		0.3721	
323.15	0.2607		0.3171		0.3744	
333.15	0.2623		0.3190		0.3766	
343.15	0.2638		0.3209		0.3789	
	[omim⁺][BF₄⁻]		[emim⁺][TfO⁻]		[bmim⁺][TfO⁻]	
293.15	0.4234	6.14	0.3112	6.08	0.3691	6.19
303.15	0.4260		0.3131		0.3714	
313.15	0.4286		0.3150		0.3737	
323.15	0.4313		0.3169		0.3760	
333.15	0.4339		0.3189		0.3784	
343.15	0.4366		0.3208		0.3808	
	[bmim⁺][OCSO₄⁻]		[bmim⁺][PF₆⁻]		[hmim⁺][PF₆⁻]	
293.15	0.5401	6.09	0.3442	6.13	0.3996	6.14
303.15	0.5434		0.3463		0.4021	
313.15	0.5467		0.3485		0.4045	
323.15	0.5500		0.3506		0.4070	
333.15	0.5534		0.3528		0.4096	
343.15	0.5568		0.3549		0.4121	
	[omim⁺][PF₆⁻]		[emim⁺][NTf₂⁻]		[bmim⁺][NTf₂⁻]	
293.15	0.4556	6.18	0.4264	6.65	0.4834	6.72
303.15	0.4584		0.4292		0.4866	
313.15	0.4612		0.4321		0.4903	
323.15	0.4641		0.4349		0.4933	
333.15	0.4670		0.4378		0.4966	
343.15	0.4699		0.4408		0.5003	
	[hmim⁺][NTf₂⁻]		[omim⁺][NTf₂⁻]		[emim⁺][EtSO₄⁻]	
293.15	0.5397	6.71	0.5959	6.78	0.3160	5.47
303.15	0.5434		0.5999		0.3177	
313.15	0.5470		0.6040		0.3195	
323.15	0.5507		0.6081		0.3212	
333.15	0.5544		0.6122		0.3230	
343.15	0.5581		0.6164		0.3248	

Table 1. Experimental values of molecular volume, V_m , and thermal expansion coefficient, α_p , of the studied ILs at temperatures T ranging from 293.15 to 343.15 K at pressure $p = 0.1$ MPa.

It is known that volume is more informative about structure and packing efficiency than density, and the conclusions and predictions obtained for volume can be immediately translated to density values. The molecular volume V_m (or formula-unit volume) of a salt is a physical observable and is defined as the sum of the ionic volumes, V_{ion} , of the constituent ions [32]. For a binary ionic liquid, V_m is given by:

$$V_m = V_{cat} + V_{an} \tag{1}$$

If we define the molecular volume (V_m) as

$$V_m = (M_w / \rho) / N_A \tag{2}$$

In Eq. (2), where M_w is the molecular weight and N_A is Avogadro’s constant, we can study the influence in V_m (see **Table 1** for numerical values) of the characteristics of the ions.

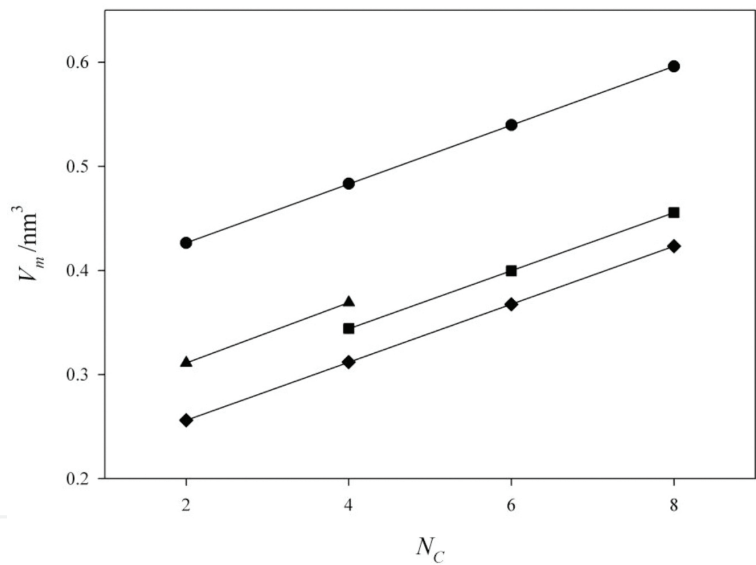


Figure 1. Dependence of the ILs’ molecular volume V_m at 293.15 K on the alkyl chain length of the cation. ● [NTf₂⁻], linear fitting: $V_m = 0.3702 + 0.02823 N_c$, $r^2 = 0.99998$; ▲ [TfO⁻], linear fitting: $V_m = 0.2533 + 0.02895 N_c$, $r^2 = 1$; ■ [PF₆⁻], linear fitting: $V_m = 0.2327 + 0.02785 N_c$, $r^2 = 0.99999$; ◆ [BF₄⁻], linear fitting: $V_m = 0.20035 + 0.02788 N_c$, $r^2 = 0.99999$.

Regarding the cations, our data (see **Figure 1** and **Table 1**) reveal a linear increase of V_m with increasing alkyl chain length, and so, with the volume of the cation. From the slope of the linear fit to dV_m/dN_c , with N_c being the number of carbons of the imidazolium alkyl chain, the volume of one methylene group ($-\text{CH}_2-$) is calculated to be $0.0281 \pm 0.0004 \text{ nm}^3$ (between 0.0279 and 0.0289 nm^3) at 293.15 K, corresponding to a molar volume of $17 \text{ cm}^3 \text{ mol}^{-1}$. These values agree well with the calculations of Kolbeck et al. [57] (0.0283 nm^3), Glasser [58] (0.0272 – 0.0282 nm^3) and Tariq et al. [39] ($17 \text{ cm}^3 \text{ mol}^{-1}$) at 298.15 K. Therefore, according to our results the increase in V_m per added methylene group is always the same, irrespective of the nature of the anion

of the ionic liquid, and, as a consequence, the volume that the cation occupies varies linearly with the number of carbons. Then, we can conclude that the length of the chain does not change significantly the interaction between ions or the packing efficiency of cations.

IL	$M_w/\text{g}\cdot\text{mol}^{-1}$	$M_{\text{Wanion}}/\text{g}\cdot\text{mol}^{-1}$	V_{an}/nm^3	$\rho_{an}/\text{g}\cdot\text{mol}^{-1}\cdot\text{nm}^{-3}$
[emim ⁺][NTf ₂ ⁻]	391.31	280.133	0.270	1035.995
[bmim ⁺][NTf ₂ ⁻]	419.37		0.287	976.073
[hmim ⁺][NTf ₂ ⁻]	447.43		0.298	940.991
[omim ⁺][NTf ₂ ⁻]	475.47		0.308	909.818
[bmim ⁺][PF ₆ ⁻]	284.18	144.961	0.148	978.144
[hmim ⁺][PF ₆ ⁻]	312.24		0.158	919.803
[omim ⁺][PF ₆ ⁻]	340.29		0.168	864.922
[emim ⁺][TfO ⁻]	260.23	149.062	0.155	960.451
[bmim ⁺][TfO ⁻]	288.29		0.173	861.132
[emim ⁺][BF ₄ ⁻]	197.97	86.802	0.100	867.153
[bmim ⁺][BF ₄ ⁻]	226.02		0.116	748.939
[hmim ⁺][BF ₄ ⁻]	254.08		0.126	691.099
[omim ⁺][BF ₄ ⁻]	282.13		0.135	641.078
[emim ⁺][EtSO ₄ ⁻]	236.29	125.126	0.160	782.037
[bmim ⁺][O ₂ SO ₄ ⁻]	348.50	209.280	0.344	608.372

Table 2. The molecular weight of the ionic liquid (M_w), molecular weight of the anion (M_{Wanion}), volume (V_{an}), and density of the molecular volume not occupied by the cation (ρ_{an}) for all investigated ILs obtained from the method proposed by Slattery et al. [32] for a temperature (T) of 293.15 K at pressure $p = 0.1$ MPa.

We can study the effect of the volume of the ion in the global V_m . The ionic volume is a measure of the size of an ion, equally valid for symmetrical and nonsymmetrical ions. But, to obtain quantitatively the volume of the constituents in an ionic liquid is not a trivial task. One way is to define the contribution of one of the ions to the molecular volume and, from Eq. (1), to obtain the other ionic volume. To do so, Slattery et al. [32] have proposed to derive the volume of the cation from crystal structures (e.g., the CCDC Database) [59] containing the ion of interest in combination with a reference ion of known volume or predicted by the contribution methods proposed by Rebelo et al. [55] and Jacquemin et al. [34, 35]. From the cationic volumes obtained by Slattery et al. [32] and our experimental molecular volume for each temperature, it is possible to assess the fraction of the molecular volume not occupied by the cation, V_{an} , and the density of it, ρ_{an} ($\rho_{an} = M_{\text{Wanion}}/V_{an}$). The values of V_m , M_w , M_{Wanion} , V_{an} and ρ_{an} are reported in **Table 2**. We think that this is not a good approximation. Ionic volume assigns a certain fraction of the total molecular volume to one of the ions. When doing so, the ionic volume is a measure not only of the volume of the actual molecular structure of the ion, but also of the interionic separation. This interionic separation must be the consequence of the interactions between

ions, mainly due to electrostatic attraction, but also of geometry of their molecular structures, their polarizability, their ability to establish some other type of interactions (i.e., hydrogen bond) and other factors. Then, it is not plausible to assume that the volume of the cation is not affected by the anion in front (like it is proposed in this method), and, at the same time, to assume that the volume of the anion changes with the cation in a very significant amount (i.e., from **Table 2**, for $[\text{BF}_4^-]$ we find a 35% increase from $[\text{emim}^+]$ to $[\text{omim}^+]$). Another question is that in this treatment the effect of temperature on the ionic volumes is not clear. Clearly, if we assume that molecular structure (i.e., covalent bonds) are temperature-independent in a certain temperature range, but an increment in T decreases density (and increases V_m), then the increment in ionic volumes should mean that the interionic distances increase. Following our argument, if there is no change in molecular structure that justifies a significant change in the geometry of packing, the main reason for the increase in the interionic distance should be a decrease in the strength of interaction, what should have other known consequences as the decrease in viscosity.

We now propose an alternative way to assign the ionic volume, and so to explain the experimental results of density. Volume of a given chemical structure can be theoretically calculated. We used the web page chemicalize.org [60] to obtain the van der Waals volume of the ions studied. This volume is not comparable with the ionic volume, because it only takes into account the isolated molecular structure and it is independent of the temperature. We propose below a way to assign the ionic volumes from the theoretically calculated volumes of the components and the experimental measurements of density, which takes into account the effect of temperature.

Cation	Structural volume/nm ³ (theoretical)	Ionic volume/nm ³ (this work)	Ionic volume/nm ³ (Slattery et al. [32])
[emim ⁺]	0.11553	0.19142	0.156
[bmim ⁺]	0.14945	0.24762	0.196
[hmim ⁺]	0.18341	0.30388	0.242
[omim ⁺]	0.21735	0.36012	0.288

Table 3. Volume of molecular structure from theoretical calculation (structure volume), ionic volume proposed in this work and ionic volume proposed by Slattery et al. [32] for the alkyl methylimidazolium cations present in the ILs studied in this work at 293.15 K at pressure $p = 0.1$ MPa.

From the values of the theoretical van der Waals volume obtained for the set of alkyl methylimidazolium cations used in this work (see **Table 3**), it is straightforward to assign a molecular volume to one methylene group ($-\text{CH}_2-$), $V_{(\text{CH}_2)\text{Theo}} = 0.01697 \pm 0.00001 \text{ nm}^3$. If we compare with the value obtained from experimental values of density at 293.15 K, $V_{(\text{CH}_2)\text{Density}} = 0.0281 \pm 0.0004 \text{ nm}^3$, the increment is 65.7%. In our hypothesis, this increment includes the fraction corresponding to the cation of interionic distance. Given that this increment is the same regardless of the length of the alkyl chain of the cation or the anion in front, it is reasonable to assume that this increment is approximately the same for the theoretically calculated volume of the whole molecule, which allows us to assign a ionic volume of the cation.

For comparison purposes, **Table 3** includes ionic volume for the cations used in this work proposed by Slattery et al. [32]. Their values are systematically lower than ours. In addition they propose a $V_{-CH_2-} = 0.023 \text{ nm}^3$, lower than ours and others found in the literature (see above). While Slattery et al. [32] proposed a constant absolute increment of ionic volume, we propose a constant percentual increment of ionic volume with alkyl chain length.

Using Eq. (1), we can obtain the ionic volume occupied by the anions at 293.15 K (see **Table 4**).

Anion	Structural volume/nm ³ (theoretical)	Ionic volume/nm ³ (this work)	% increment
[BF ₄ ⁻]	0.05420	0.0634 ± 0.0008	17
[PF ₆ ⁻]	0.07135	0.0952 ± 0.0007	33
[TfO ⁻]	0.08520	0.1201 ± 0.0010	41
[EtSO ₄ ⁻]	0.09639	0.1242	29
[NTf ₂ ⁻]	0.15671	0.2349 ± 0.0002	50
[OcSO ₄ ⁻]	0.19820	0.2919	47

Table 4. van der Waals volume of molecular structure from theoretical calculation (structural volume) and ionic volume proposed in this work for anions present in the ILs studied at 293.15 K at pressure $p = 0.1 \text{ MPa}$.

We find various advantages in this procedure. First, we are able to obtain a plausible ionic volume for the anions participating in the ionic liquid studied. Our results show that the ionic volume of the anion is not affected significantly by the length of the alkyl chain of the cation.

The second consequence of our approximation is that there is a very good correlation between the molecular volume with both, volume of the cation and also with the volume of the anion.

Indeed, in **Figure 2**, we observe that volume of the anion is the fundamental factor to determine the molecular volume (the higher the volume of the anion, the higher V_m). According to theoretical calculations (**Table 4**), the order of volumes is: [OcSO₄⁻] > [NTf₂⁻] > [EtSO₄⁻] > [TfO⁻] > [PF₆⁻] > [BF₄⁻]. As we mentioned before, it is very likely that some other factors (geometry of the anion, distribution of charge,...) have some influence in the global volume, but according to our results their importance is smaller than the volume of the anion. These data explain the trend observed in the experimental values of the density.

Using our treatment, we can obtain the increment of anionic volume with respect to the theoretical volume of the molecular structure (**Table 4**). This increment takes into account interionic distances and effect of temperature and could be taken as a measure of the packing quality. If we assume this idea, we conclude that packing quality is higher for small molecules, but when the size of the anion becomes similar to the cation, the packing quality decreases, reaches a certain level and probably other factors than volume become significant.

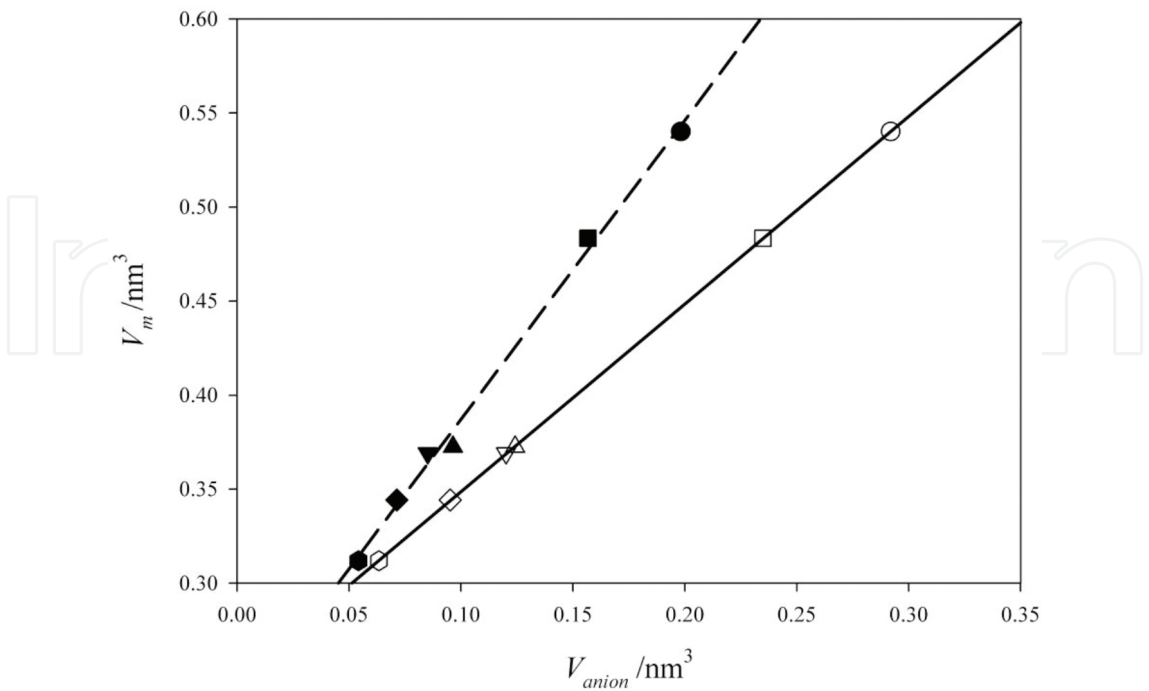


Figure 2. Molecular volume at 293.15 K of ILs based on [bmim⁺] versus volume of anion. ● [OCSO₄⁻]; ■ [NTf₂⁻]; ▲ [EtSO₄⁻]; ▼ [TfO⁻]; ◆ [PF₆⁻]; ● [BF₄⁻]. V_m for [bmim⁺][EtSO₄⁻] is not measured but predicted. Full symbols are for van der Waals theoretically calculated anionic volume. Empty symbols are for our proposed ionic volume obtained from averages over experimental measurements of density (**Table 4**). In this plot, standard deviations are smaller than symbols. Fitting results: - - - theoretical volume $V_m = 1.592 V_{an} + 0.2279 \text{ nm}^3$, $r^2 = 0.9956$. — — — ionic volumes $V_m = 0.9980 V_{an} + 0.2489 \text{ nm}^3$, $r^2 = 0.99999$.

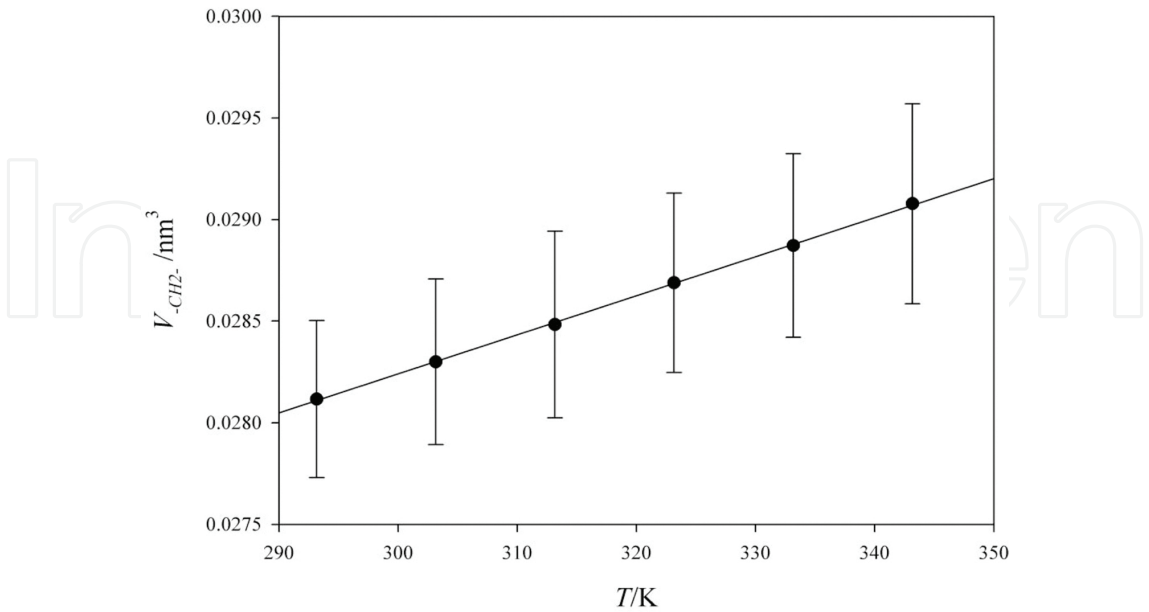


Figure 3. Dependence of the ionic volume of $-\text{CH}_2-$ ionic (obtained from density experimental values) on temperature. All numerical data can be found in **Table 6**. Linear fit: $V_{\text{CH}_2-} = 0.02247 + 1.922 \times 10^{-5} T$; $r^2 = 0.9996$.

Finally, this treatment allows us to predict with high accuracy the densities of all the combinations at all temperatures of these anions and cations by obtaining molecular volumes of ILs after assigning proper ionic volumes to its constituents. Indeed, following the method we have used for $T = 293.15$ K for the rest of temperatures studied, we obtain (see **Figure 3**) a linear dependence $V_{CH_2} = 1.922 \times 10^{-5} T + 0.02247 \text{ nm}^3$ ($r^2 = 0.9996$) of the ionic volume of CH_2 with temperature (numerical values in **Table 5**).

T/K	Ionic volume/ nm^3	S.D.	% increase
293.15	0.0281	0.0004	65.7
303.15	0.0283	0.0004	66.8
313.15	0.0285	0.0005	67.8
323.15	0.0287	0.0004	69.1
333.15	0.0289	0.0005	70.1
343.15	0.0291	0.0005	71.3

% increase = $32.83 + 0.112 T$; $r^2 = 0.9990$.

Table 5. Effect of temperature (T) on ionic volume of $-CH_2-$ and % of increase over theoretically calculated van der Waals volume.

Knowing this quantitative dependence the ionic volume of alkyl imidazolium cations with different alkyl chain lengths can be properly assigned for any temperature. We propose the following equation:

$$V_{al-imid} = V_{al-imid-theo} (1.328 + 1.120 \times 10^{-3} T) \quad (3)$$

Or in terms of number of carbons

$$V_{al-imid} = (0.08159 + 0.01697 N_C) (1.328 + 1.120 \times 10^{-3} T) \quad (4)$$

In Eq. (3), $V_{al-imid}$ is the ionic volume of any alkyl imidazolium cation and $V_{al-imid-theo}$ is the calculated theoretical van der Waals volume, both in nm^3 . In Eq. (4), N_C is the number of carbons and T is the temperature in Kelvin. Although the limits of validity should be established it is likely that the range of application of these equations is rather broad.

Regarding the dependence of the ionic volumes of the anions studied in this work on temperature, in all cases we find a very good linear dependence, with a tendency to higher slopes for higher ionic volumes (see **Figure 4** and **Table 6** for numerical values). From our results, the ionic volume of these ions can be predicted for any temperature:

$$V_{BF_4} = V_{BF_4theo} (1.083 + 0.365 \times 10^{-3} T) = 0.0587 + 1.98 \times 10^{-5} T \tag{5}$$

$$V_{PF_6} = V_{PF_6theo} (1.171 + 0.596 \times 10^{-3} T) = 0.0835 + 4.25 \times 10^{-5} T \tag{6}$$

$$V_{NTf_2} = V_{NTf_2theo} (1.201 + 1.032 \times 10^{-3} T) = 0.1882 + 16.17 \times 10^{-5} T \tag{7}$$

$$V_{TfO} = V_{TfOtheo} (1.200 + 0.738 \times 10^{-3} T) = 0.1022 + 6.29 \times 10^{-5} T \tag{8}$$

$$V_{EtSO_4} = V_{EtSO_4theo} (1.156 + 0.468 \times 10^{-3} T) = 0.1114 + 4.51 \times 10^{-5} T \tag{9}$$

$$V_{OctSO_4} = V_{OctSO_4theo} (1.233 + 0.829 \times 10^{-3} T) = 0.0835 + 16.44 \times 10^{-5} T \tag{10}$$

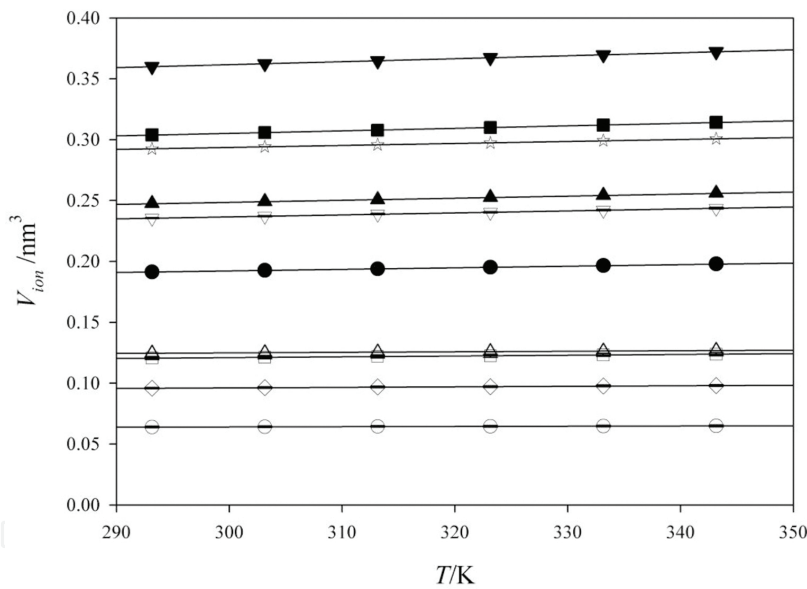


Figure 4. Ionic volume (V_{ion}) versus temperature (T). This figure shows the linear dependence of ionic volume on temperature, which is higher for bigger structures. All numerical data (including fitting parameters) can be found in **Table 6**. ● [emim⁺]; ▲ [bmim⁺]; ■ [hmim⁺]; ▼ [omim⁺]; ○ [BF₄⁻]; ▽ [NTf₂⁻]; □ [TfO⁻]; ▲ [EtSO₄⁻]; ◇ [PF₆⁻]; ★ [OcSO₄⁻].

In Eqs. (5–10), V_{anion} is the ionic volume of each anion and $V_{anion-theo}$ is the calculated theoretical van der Waals volume, both in nm³. T is the temperature in Kelvin.

To check our procedure we have compared the calculated densities from Eqs. (1–10) with our experimental values and some others found in the literature [34, 39, 40, 61–68]. As an illustration, some results are plotted in **Figure 5** (see also **Tables 7** and **8** for numerical values).

<i>T</i> /K	[emim ⁺]	[bmim ⁺]	[hmim ⁺]	[omim ⁺]	[BF ₄ ⁻]	[NTf ₂ ⁻]	[TfO ⁻]	[EtSO ₄ ⁻]	[PF ₆ ⁻]	[OctSO ₄ ⁻]
293.15	0.1914	0.2476	0.3039	0.3601	0.0640	0.2356	0.1206	0.1246	0.0959	0.2925
303.15	0.1927	0.2492	0.3059	0.3625	0.0642	0.2372	0.1213	0.1250	0.0964	0.2942
313.15	0.1939	0.2508	0.3078	0.3648	0.0644	0.2390	0.1220	0.1256	0.0969	0.2959
323.15	0.1953	0.2527	0.3101	0.3674	0.0645	0.2404	0.1225	0.1259	0.0972	0.2973
333.15	0.1966	0.2543	0.3121	0.3698	0.0648	0.2421	0.1232	0.1264	0.0978	0.2991
343.15	0.1980	0.2506	0.3143	0.3724	0.0649	0.2437	0.1238	0.1268	0.0980	0.3007
<i>a</i> × 10 ³ /nm ³ · K ⁻¹	0.1309	0.1693	0.2078	0.2462	0.0198	0.1617	0.0629	0.0451	0.0425	0.1644
<i>b</i> /nm ³	0.1530	0.1979	0.2829	0.2878	0.0587	0.1882	0.1022	0.1114	0.0835	0.2443
<i>r</i> ²	0.9996	0.9996	0.9996	0.9996	0.9828	0.9994	0.9979	0.9962	0.9924	0.9997

Table 6. Dependence of the ionic volumes (in nm³) of all the ions studied in this work on the temperature (*T*). Fitting parameters to equation $V_{ion} = aT + b$ are also included.

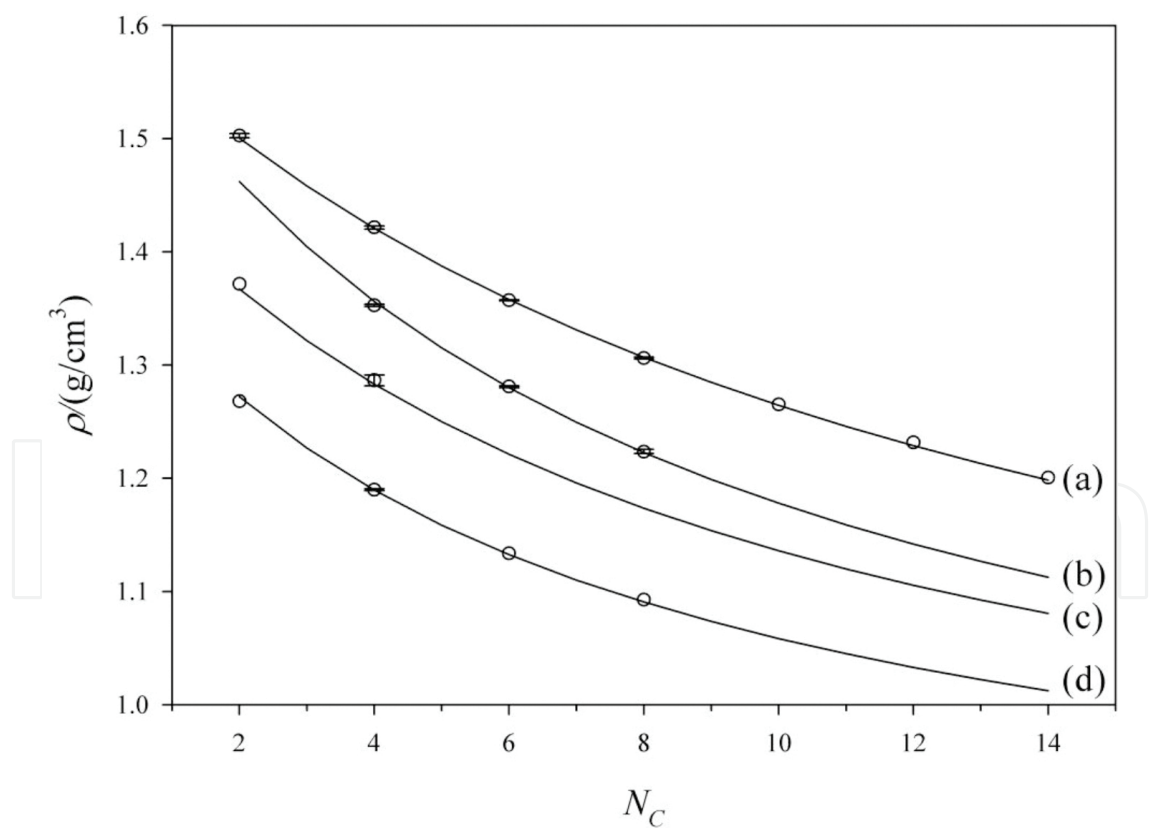


Figure 5. Density at 313.15 K of different ILs versus number of carbons of the alkyl chain of the cation. The anions are: (a) [NTf₂⁻]; (b) [PF₆⁻]; (c) [TfO⁻]; (d) [BF₄⁻]. ○ Experimental (averaged from different sources, see Table 8 for numerical values); (— —) predicted from Eqs. (5–10). For experimental values, the error bars are smaller than the size of the symbol.

$\rho/(\text{g}/\text{cm}^3)$											
Experimental (different sources)						Exp. Average $\pm \sigma$		Predicted	Error*	Error+	
[NTf ₂ ⁻]											
[emim ⁺]	1.5238 ¹	1.5197 ²	1.5229 ³	1.5234 ³	1.5260 ⁴	1.5232	0.0023	1.5215	-0.0016	-0.11	
[bmim ⁺]	1.4403 ¹	1.4408 ²	1.4427 ³	1.4402 ³	1.4389 ⁵ 1.4405 ⁵	1.4406	0.0012	1.4408	0.0003	0.02	
[hmim ⁺]	1.3763 ¹	1.3755 ²	1.3751 ³	1.3754 ⁶	1.3750 ⁶	1.3755	0.0005	1.3770	0.0015	0.11	
[omim ⁺]	1.3248 ¹	1.3234 ²	1.3245 ³	1.3281 ⁴		1.3252	0.0020	1.3251	-0.0001	-0.01	
[c ₁₀ mim ⁺]		1.2828 ²	1.2824 ³			1.2826	0.0003	1.2821	-0.0005	-0.04	
[c ₁₂ mim ⁺]		1.2490 ²				1.2490		1.2459	-0.0031	-0.25	
[PF ₆ ⁻]											
[bmim ⁺]	1.3707 ¹	1.3679 ²	1.3698 ³	1.3681 ³	1.3704 ⁵ 1.3716 ^{7,8}	1.3698	0.0015	1.3734	0.0036	0.26	
[hmim ⁺]	1.2973 ¹	1.2964 ²	1.2979 ^{7,8}			1.2972	0.0008	1.2964	-0.0008	-0.06	
[omim ⁺]	1.2402 ¹	1.2378 ²	1.2396 ^{7,8}			1.2392	0.0012	1.2385	-0.0007	-0.06	
[BF ₄ ⁻]											
[emim ⁺]	1.2833 ¹					1.2833		1.2869	0.0036	0.28	
[bmim ⁺]	1.2031 ¹	1.2029 ²	1.2049 ^{3,9}	1.2038 ³		1.2037	0.0009	1.2041	0.0004	0.04	
[hmim ⁺]	1.1475 ¹					1.1475		1.1467	-0.0008	-0.07	
[omim ⁺]	1.1064 ¹					1.1064		1.1044	-0.0020	-0.18	
[TfO ⁻]											
[emim ⁺]	1.3884 ¹					1.3884		1.3848	-0.0036	-0.26	
[bmim ⁺]	1.2966 ^x	1.3035 ²	1.3013 ³	1.2900 ¹⁰		1.2979	0.0060	1.2998	0.0019	0.15	
¹ This work.											
² Tariq et al. [39].											
³ Jacquemin et al. [34].											
⁴ Gardas et al. [63].											
⁵ Troncoso et al. [64].											
⁶ Łachwa et al. [65].											
⁷ Pereiro and Rodríguez [66];											
⁸ Pereiro and Rodríguez [67].											
⁹ Iglesias-Otero et al. [62].											
¹⁰ Bonhôte et al. [68].											
* Error, in g/cm ³ .											
+ Error, in %.											

Table 7. Comparison of predicted (this work) and experimental (different sources) densities (ρ) for different ILs at temperature $T = 293.15$ K at pressure $p = 0.1$ MPa.

$\rho/(\text{g}/\text{cm}^3)$										
Experimental (different sources)						Exp. Average $\pm \sigma$		<i>Predicted</i>	<i>Error</i> [*]	<i>Error</i> [*]
[NTf ₂ ⁻]										
[emim ⁺]	1.5037 ¹	1.4996 ²	1.5029 ³	1.5034 ³	1.5038 ⁴	1.5027	0.0018	1.5005	-0.0022	-0.15
[bmim ⁺]	1.4202 ¹	1.4216 ²	1.4230 ⁶	1.4198 ⁵	1.4214 ⁵	1.4235 ³	1.4212 ³	1.4215	0.0015	-0.0005
[hmim ⁺]	1.3580 ¹	1.3572 ²	1.3569 ³	1.3570 ⁶				1.3573	0.0005	1.3581
[omim ⁺]	1.3070 ¹	1.3055 ²	1.3070 ³	1.3056 ⁴				1.3063	0.0008	1.3070
[c ₁₀ mim ⁺]		1.2653 ²	1.2653 ³					1.2653	0.0000	1.2646
[c ₁₂ mim ⁺]		1.2318 ²						1.2318		1.2289
[c ₁₄ mim ⁺]		1.2006 ²						1.2006		1.1985
[PF ₆ ⁻]										
[bmim ⁺]	1.3540 ¹	1.3513 ²	1.3533 ³	1.3518 ³	1.3534 ⁵	1.3528 ⁷		1.3528	0.0010	1.3562
[hmim ⁺]	1.2815 ¹	1.2804 ²						1.2810	0.0008	1.2801
[omim ⁺]	1.2250 ¹	1.2224 ²						1.2237	0.0018	1.2227
[BF ₄ ⁻]										
[emim ⁺]	1.2681 ¹							1.2681		1.2721
[bmim ⁺]	1.1905 ¹	1.1887 ²	1.1901 ³	1.1889 ³	1.1908 ⁶	1.1907 ⁸		1.1900	0.0009	1.1898
[hmim ⁺]	1.1337 ¹							1.1337		1.1328
[omim ⁺]	1.0929 ¹							1.0929		1.0908
[TfO ⁻]										
[emim ⁺]	1.3716 ¹							1.3716		1.3673
[bmim ⁺]	1.2808 ¹	1.2877 ²	1.2856 ³	1.2924 ⁷				1.2866	0.0048	1.2832

¹This work.

²Tariq et al. [39].

³Jacquemin et al. [34].

⁴Gardas et al. [63].

⁵Troncoso et al. [64].

⁶Gomes de Azevedo et al. [61].

⁷Soriano et al. [40].

⁸Iglesias-Otero et al. [62].

^{*}Error, in g/cm³.

^{*}Error, in %.

¹This work.

²Tariq et al. [39].

³Jacquemin et al. [34].

⁴Gardas et al. [63].

⁵Troncoso et al. [64].

⁶Gomes de Azevedo et al. [61].

⁷Soriano et al. [40].

⁸Iglesias-Otero et al. [62].

*Error, in g/cm³.

*Error, in %.

Table 8. Comparison of predicted (this work) and experimental (different sources) densities (ρ) for different ILs at temperature $T = 313.15$ K at pressure $p = 0.1$ MPa.

Tariq et al. [39] showed the experimental density of some ILs composed with combinations of cations and anions not used for our research group. A further test for our method is to predict volumes of these ions. For $T = 293.15$ K, we obtain the volume of methylsulfate ([MeSO₄⁻]) and acetate ([OAc⁻]): $V_{\text{MeSO}_4} = 0.0956$ nm³; $V_{\text{OAc}} = 0.0640$ nm³. The volume of the trihexyl(tetradecyl)phosphonium cation ([P_{6 6 6 14}⁺]) can be obtained from data of three different ILs: [P_{6 6 6 14}⁺][NTf₂⁻]; [P_{6 6 6 14}⁺][TfO⁻]; [P_{6 6 6 14}⁺][OAc⁻]. We obtain $V_{[\text{P}_{6 6 6 14}^+] } = 0.945 \pm 0.002$ nm³. We can see that

although $[P_{6,6,14}^+][OAc^-]$ is formed by two anions not used to obtain the equations proposed in this work, the result obtained is very close to the ones obtained from the other ILs.

To have an idea of the quality of the predictions we can use the average deviation from experimental values. Then, we can compare our values (see **Tables 7 and 8**) with those obtained by Tariq et al. [39]. Those average deviations are between $\sigma_{ave} = 0.21$ and $\sigma_{ave} = 1.29$. Our method gives $\sigma_{ave} = 0.13$.

As a summary, with our results we should be able to predict, prior to synthesis, the density and molecular volumes for IL with alkyl imidazolium cations and with different anions (and very likely combinations of ions of similar chemical structure) in a wide range of temperatures from easily accessible theoretical calculations of the structure of the proposed ions.

2.5. Estimation by correlations between density and other properties

The last approach to estimate density is through correlations between density and other properties. Obviously, no prediction can be obtained if these correlations have not been previously established. But these methods can be especially interesting if the measurement of the property used is easier or cheaper than the measurement of the density. A good example is the refractive index.

There are some authors who have studied the relationship between density and refractive index in order to predict one of the properties from the other one due to the experimental measurement of refractive index only needs a drop of the ionic liquid and it is very fast. However, in the case of density the determination requires higher volumes of ionic liquid and it takes more time. Tariq et al. [39] and Soriano et al. [38, 40] used different empirical models (Lorentz-Lorenz, Dale-Gladstone, Eykman, Oster, Arago-Biot and Newton equations) to predict density of ILs from their refractive index. Other authors such as Deetlefs et al. [41] and Gardas et al. [42] used the parachor to estimate density. Parachor is a surface-tension-weighted molar volume, which constitutes a link between the structure, density and surface tension of the ILs. Deetlefs et al. [41] also used the refraction molar to estimate density.

We detail in the following paragraphs our prediction of the density from the refractive index.

It is known that the density and refractive index (n) were correlated using several empirical equations of the form:

$$f(n) = k\rho \quad (11)$$

where $f(n)$ is a function of the refractive index, k is an empirical constant that depends on the liquid and the wavelength at which the refractive index is measured and ρ is the density of the liquid. The $f(n)$ function is associated with several empirical equations. In this work, we have used the most common equations, those of Lorentz-Lorenz (Eq. (12)), Dale-Gladstone (Eq. (13)), Eykman (Eq. (14)), Oster (Eq. (15)), Arago-Biot (Eq. (16)) and Newton (Eq. (17)), which have also been used by different authors to correlate the density with the refractive index.

$$f(n) = (n^2 - 1) / (n^2 + 2) \quad (12)$$

$$f(n) = (n - 1) \quad (13)$$

$$f(n) = (n^2 - 1) / (n + 0.4) \quad (14)$$

$$f(n) = (n^2 - 1)(2n^2 + 1) / n^2 \quad (15)$$

$$f(n) = n \quad (16)$$

$$f(n) = n^2 - 1 \quad (17)$$

System	L-L	D-G	Eykman	Oster	A-B	Newton
[emim ⁺][BF ₄ ⁻]	0.1948	0.3220	0.4289	1.9418	1.1130	0.7752
[bmim ⁺][BF ₄ ⁻]	0.2125	0.3524	0.4687	2.1276	1.1966	0.8518
[hmim ⁺][BF ₄ ⁻]	0.2251	0.3738	0.4969	2.2585	1.2586	0.9055
[omim ⁺][BF ₄ ⁻]	0.2359	0.3923	0.5212	2.3719	1.3102	0.9523
[emim ⁺][TfO ⁻]	0.1881	0.3128	0.4155	1.8914	1.0442	0.7594
[bmim ⁺][TfO ⁻]	0.2027	0.3375	0.4481	2.0415	1.1208	0.8204
[bmim ⁺][O ₂ CSO ₄ ⁻]	0.2620	0.4407	0.5825	2.6791	1.3885	1.0865
[bmim ⁺][PF ₆ ⁻]	0.1813	0.2996	0.3992	1.8059	1.0404	0.7203
[hmim ⁺][PF ₆ ⁻]	0.1947	0.3224	0.4291	1.9450	1.1052	0.7775
[omim ⁺][PF ₆ ⁻]	0.2061	0.3418	0.4546	2.0638	1.1607	0.8263
[emim ⁺][NTf ₂ ⁻]	0.1679	0.2784	0.3703	1.6809	0.9457	0.6729
[bmim ⁺][NTf ₂ ⁻]	0.1789	0.2969	0.3947	1.7933	1.0031	0.7186
[hmim ⁺][NTf ₂ ⁻]	0.1888	0.3137	0.4168	1.8959	1.0526	0.7605
[omim ⁺][NTf ₂ ⁻]	0.1969	0.3275	0.4350	1.9797	1.0952	0.7946
[emim ⁺][EtSO ₄ ⁻]	0.2286	0.3853	0.5088	2.3446	1.2020	0.9525
S.D.	0.0032	0.0020	0.0025	0.0016	0.0099	0.0018

Table 9. Parameters $k/\text{cm}^3\cdot\text{g}^{-1}$ for the different empirical equations from Eq. (6) for the equations proposed by Lorentz-Lorenz (L-L), Dale-Gladstone (D-G), Eykman, Oster, Arago-Biot (A-B) and Newton.

All these equations assume that the relation between density and refractive index is temperature-independent. But, from our results (see **Tables 1** and **9**) it can be deduced that k in Eq. (11) has a certain dependence on T (as it is illustrated below in **Figure 5** in the case of Eq. (16)).

Nevertheless, as a first approximation, and assuming that the dependence is small, it is worth finding the equation that best fits our experimental results. In this approximation we shall assume that $k=f(n)\rho$ only depends on the nature of ionic liquid. The value for each ionic liquid is obtained as the average for all the temperatures. The standard deviation is obtained as described in Eq. (18). From these calculations (**Table 9**), we conclude that the Oster equation is the one that best fitted our experimental results.

$$S.D=\left[\frac{\sum(z_{\text{exp}}-z_{\text{calc}})^2}{n}\right]^{\frac{1}{2}}\tag{18}$$

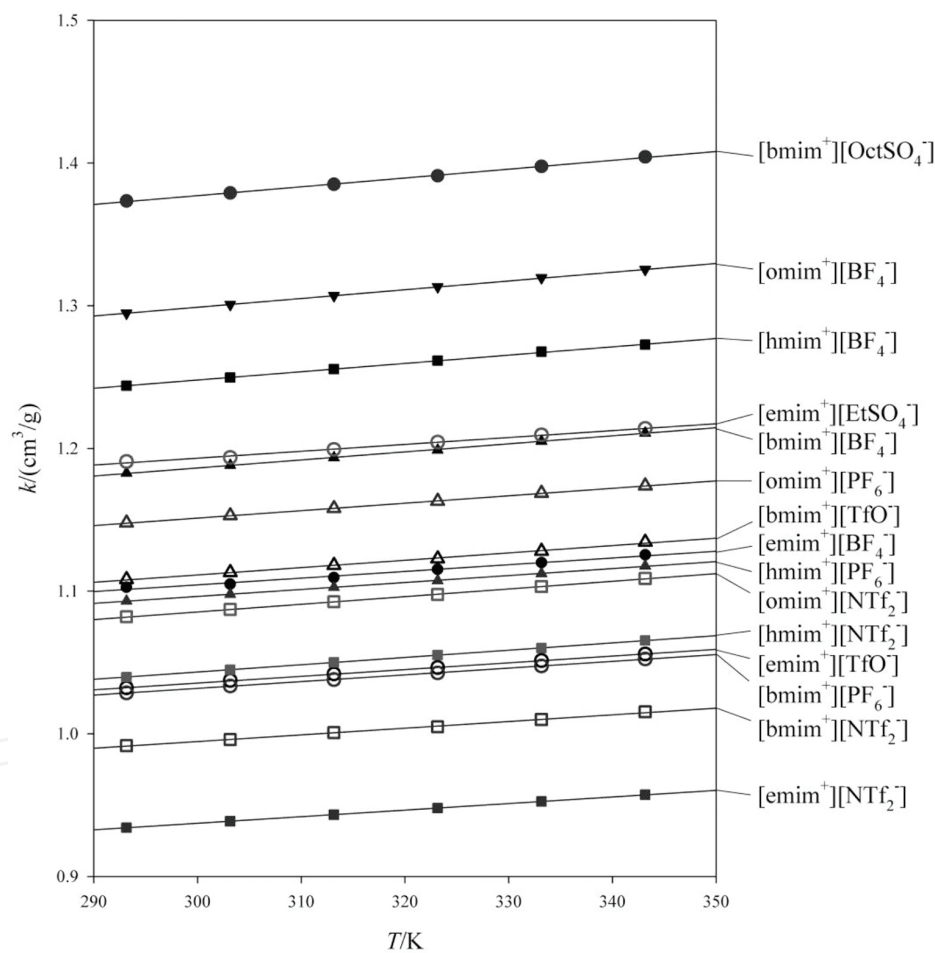


Figure 6. Values of $k = n/\rho$ of different ILs for different temperatures. Parameters for linear fitting can be found in **Table 10**.

As mentioned above, a small dependence of k on T can be observed from our experimental results, and, as a consequence, we used another approach, defining $k = n/\rho$ and fitting the results to a linear equation in the form $k = k_0T + k_1$. **Figure 6** (numerical values can be found in **Table 10**) shows the good quality of the fittings.

ILs	$k_0 \times 10^4/\text{cm}^3\cdot\text{g}^{-1}\cdot\text{K}^{-1}$	$k_1/\text{cm}^3\cdot\text{g}^{-1}$	r^2	S.D.
[emim ⁺][BF ₄ ⁻]	4.709	0.9632	0.9882	0.0009
[bmim ⁺][BF ₄ ⁻]	5.632	1.0174	0.9992	0.0003
[hmim ⁺][BF ₄ ⁻]	5.829	1.0731	0.9994	0.0002
[omim ⁺][BF ₄ ⁻]	6.139	1.1149	0.9999	0.0001
[emim ⁺][TfO ⁻]	4.712	0.8942	0.9996	0.0002
[bmim ⁺][TfO ⁻]	5.140	0.9572	0.9971	0.0005
[bmim ⁺][O ₃ SO ₄ ⁻]	6.189	1.1916	0.9991	0.0003
[bmim ⁺][PF ₆ ⁻]	4.717	0.8904	0.9998	0.0001
[hmim ⁺][PF ₆ ⁻]	4.888	0.9496	0.9997	0.0001
[omim ⁺][PF ₆ ⁻]	5.221	0.9946	0.9997	0.0001
[emim ⁺][NTf ₂ ⁻]	4.622	0.7986	1.0000	0.00003
[bmim ⁺][NTf ₂ ⁻]	4.695	0.8538	0.9981	0.0003
[hmim ⁺][NTf ₂ ⁻]	5.123	0.8896	0.9999	0.0001
[omim ⁺][NTf ₂ ⁻]	5.351	0.9250	0.9997	0.0002
[emim ⁺][EtSO ₄ ⁻]	4.831	1.0482	0.9952	0.0006
			Average	0.0003

Table 10. Fitting parameters for $k = n/\rho$ (n , refractive index, ρ density) of ILs studied to a linear equation ($k = k_0T + k_1$).

As a consequence, we think that a very good and simple description of the correlation between density and the refraction index can be obtained by including the dependence on T . If we compare the S.D. results with those in **Table 9** for any of the equations proposed, a substantial improvement in the quality of the fitting can be observed. Given the quality of the data, once the quantitative relation between density and refractive index is known in a range of temperatures, it is possible just to measure one of these properties at any temperature (probably even outside the range) to know the value of the other with a high degree of precision.

3. Prediction methods of refractive index of ionic liquids

The refractive index (n) can be defined as the ratio of the speed of light in vacuum to that in a given medium [69]. Research studies focused on the modeling and even on the measurement of the refractive index of ILs are scarce in the literature even though its measurement is very simple and fast [9]. However, due to the high number of potential ILs we think it is substantially relevant to develop methods to estimate the refractive index of ILs prior to synthesis.

Some of the studies related to the estimation of refractive index are listed here. The first prediction model in the literature was developed by Deetlefs et al. [41]. They calculated the mo-

lar refraction to predict the refraction indices of ILs from their surface tension. However, all the parameters involved in this model should be experimentally measured or correlated with other experimental properties; thus, it is not suitable to predict refractive indices of new ILs. In addition, it was developed only from 9 ILs so it is far away of being a universal method. The next model was published by Gardas and Coutinho [10] who developed a GCM to predict refractive index of ILs from 245 experimental values of refractive index of ILs in the temperature range from 283.15 to 363.15 K. All the ILs used to model the refractive index were based on imidazolium salts (with different anions) thus this model is not appropriate to estimate the refractive index of ILs with another cation. The same method was used by Freire et al. [70] and Soriano et al. [38] who broadened the method by incorporating some new ILs. Xu et al. [71] synthesized a new ionic liquid ($[C_3mim][Val]$) and measured its refractive index in the temperature range of 298.15–333.15 K. After that, they estimated the refractive index for the homologue ILs ($[C_nmim][Val]$; $n = 2, 4, 5, 6$) following the same procedure than Deetlefs et al. [41]. This model is also very limited because it was developed only for a specific family of ILs. Finally, Sattari et al. [9] tried to solve the limitations of the rest of the predictive models of refractive index of ILs developing a widely applicable model based on a QSPR method using genetic function approximation (GFA). They used experimental data of 82 ILs with a great variety of structures and developed a 9-parameter model with very good prediction results.

4. Conclusions

Many efforts have been done during the last years to develop a great variety of prediction methods of density of ILs. Thus they have reached a high degree of perfection. Prediction methods of density of ILs can be classified in five categories although the methods are sometimes a combination of more than one category: i) QSPR, ii) ANN, iii) EoS, iv) GCM, and v) correlations between density and other properties.

QSPR models are based on quantum chemistry calculations and this is their great advantage and, at the same time, their main drawback. While virtually any imagined compound can be studied with no previous experimental knowledge, usually the calculations are not easy and only can be developed by very specialized research groups.

ANN is an especially efficient computer algorithm whose main advantage is that it is usually suitable to model chemical properties whose behavior is highly nonlinear because nonlinear relationships are well described with ANN. However, the predicting capabilities of this method depend on the quality of the algorithm for learning and very importantly on the quality, quantity and nature of experimental (or calculated) data used for the learning process.

Equations of state are well known for determining the relationship between pressure, temperature, volume and composition of components providing a theoretical way to calculate some physical properties such as density. The main advantage of this method is the simplicity in their use but a possible drawback is that to obtain the density of the desired compound

usually some previous experimental (or calculated) data of certain critical properties (temperature, pressure, volume,...) are needed.

In the GCM methods, the desired property is obtained as individual contribution of each of the components of the final compound. Then, predictions are obtained using available simple equations. The main drawback of these methods is that their predictive capability depends on previous experimental (or calculated) data. With some exceptions, it is impossible to predict density if no data are available for both of the components of an ionic liquid. On the other hand, usually good predictions can be obtained very easily for any combination of known counterions in a few minutes.

Estimating the density of ILs by correlations between this property and other physical properties is especially interesting if the measurement of the property used is easier or cheaper than the measurement of the density like in the case of refractive index. Nevertheless, the main drawback is that no prediction can be obtained if previous correlations have not been properly established.

Our method provides a fast and simple way to predict the density of ILs with alkyl imidazolium cations and with different anions (and very likely combinations of ions of similar chemical structure) based on the molecular volume in a wide range of temperatures from simple theoretical calculations of the structure of the proposed ions.

The correlation between density and the refraction index is usually described in the literature by equations which are assumed to be temperature-independent; we have shown that a substantial improvement can be obtained if the dependence on temperature is included.

Prediction of refractive index of ILs has not been so widely studied in the literature like in the case of density because the relationships between this property and the ion constituents of the ILs are not so direct and accessible. For this reason, more studies in this field are required.

We support the idea that ILs can be designed with adjustable properties (at least density and refractive index, but very probably some others) based on the structure of the cation and anion chosen. Our method may provide valuable contributions for the design and study of present and future ILs.

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Author details

Mercedes G. Montalbán¹, Mar Collado-González², F. Guillermo Díaz-Baños² and Gloria Villora^{1*}

*Address all correspondence to: gvillora@um.es

1 Department of Chemical Engineering, Faculty of Chemistry, Regional Campus of International Excellence "Campus Mare Nostrum," University of Murcia, Murcia, Spain

2 Department of Physical Chemistry, Faculty of Chemistry, Regional Campus of International Excellence "Campus Mare Nostrum," University of Murcia, Murcia, Spain

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